

**UNCLASSIFIED**

**AD 410329**

**DEFENSE DOCUMENTATION CENTER**

**FOR**

**SCIENTIFIC AND TECHNICAL INFORMATION**

**CAMERON STATION, ALEXANDRIA, VIRGINIA**



**UNCLASSIFIED**

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

N-63-4-3

BSD-TDR-63-105

REPORT NO.  
TDR-169(S3153-01)TN-5

①

AD No. 410329  
DDC FILE COPY

410329

## A Literature Survey of Ions in Flames

15 JUNE 1963

*Prepared by*

S. A. GREENE

AEROSPACE MECHANICS

SUBDIVISION

*Scale*

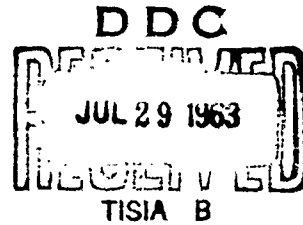
*Prepared for* COMMANDER

HEADQUARTERS, BALLISTIC SYSTEMS DIVISION

AIR FORCE SYSTEMS COMMAND

UNITED STATES AIR FORCE

*Norton Air Force Base, California*



AEROSPACE CORPORATION

CONTRACT NO. AF 04(695)-169

410329

4.60

18  
4 4.00  
19  
BSD TDR 63 105

5 17505 7+9 NA

14  
Regt. No.  
TDR 169/S3153/01/TN/5

6

A LITERATURE SURVEY OF IONS IN FLAMES,

10 Prepared by  
S. A. Greene.  
Aerospace Mechanics  
Subdivision

20 16

21 NA

for

AEROSPACE CORPORATION  
San Bernardino Operations

16 + 17 NA

15

Contract AF 04/695-169

11


15 Jun 63,


12 37p. 13 NA


Prepared for  
COMMANDER  
HEADQUARTERS, BALLISTIC SYSTEMS DIVISION  
AIR FORCE SYSTEMS COMMAND  
UNITED STATES AIR FORCE  
Norton Air Force Base  
California

Report No.  
TDR-169(S3153-01)TN-5

A LITERATURE SURVEY OF IONS IN FLAMES


Prepared by   
S. A. Greene  
Aerospace Mechanics  
Subdivision

Approved by   
Kenneth Pearce  
Group Director  
Re-Entry Systems Group


Approved by   
for Darwin C. Middlekauff  
Col. USAF  
Deputy for Ballistic Missile  
Re-Entry Systems

Prepared for  
  
COMMANDER  
HEADQUARTERS, BALLISTIC SYSTEMS DIVISION  
AIR FORCE SYSTEMS COMMAND  
UNITED STATES AIR FORCE  
Norton Air Force Base  
California

# ABSTRACT



The literature on the <sup>p</sup>ions in flames<sup>ne</sup> aspects of combustion in laboratory flames was reviewed. The nature of excess non-equilibrium ionization and rates of ionization are discussed. Rates for positive ion decay are presented as well as the effects of electronegative gases on amounts of ionization, rates of positive ion and electron decay, and rates of electron attachment.



## CONTENTS

ABSTRACT . . . . .	v
SUMMARY . . . . .	xiii
LIST OF SYMBOLS . . . . .	xv
I. INTRODUCTION . . . . .	1
II. ION CONCENTRATIONS IN FLAMES . . . . .	3
III. NATURE OF EXCESS IONIZATION . . . . .	5
IV. IDENTIFICATION OF IONS IN HYDROCARBON FLAMES . . . . .	7
V. RATES OF PRODUCTION OF POSITIVE IONS . . .	9
VI. TRANSMITTED CHEMI-IONIZATION . . . . .	11
VII. POSITIVE ION RECOMBINATION IN FLAMES . . .	13
VIII. EFFECT OF ELECTRONEGATIVE GASES ON FLAME IONS . . . . .	17
BIBLIOGRAPHY . . . . .	23

## TABLES

I.	Equilibrium Combustion Products of the Stoichiometric Cyclohexane/Air Flame (2200K) . . . . .	26
II.	Possible Chemi-ionization Reactions . . . . .	27
III.	Rates of Ion Formation in Propane/Air Flames . . . .	28
IV.	Electron Affinities . . . . .	29
V.	Effect of Carbon Tetrachloride in Reducing Free-Electron Concentrations (Ne) in a Carbon Monoxide/Air Flame at 1 Atm and a Flame Temperature of 2000K . . . . .	30
VI.	Effect of Carbon Tetrachloride on Recombination Rates of Alkali-metal Ions in a Propane/Air Flame at 1 Atm and a Flame Temperature of 1840K . . . . .	31

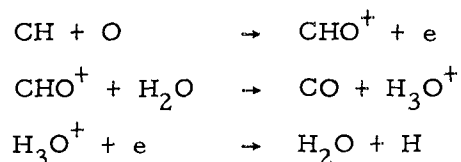


## FIGURES

1.	Typical Plot of Ion Concentration in a Laboratory Flame . . . . .	32
2.	Ion Concentration Profiles for an Acetylene/Oxygen Flame . . . . .	33
3.	Effect of Chlorine on Recombination in a Propane/Air Flame at 1.0 atm . . . . .	34
4.	First Order Plot of Electron Disappearance in a Stoichiometric Propane/Air Flame at 1.0 atm. . . . .	35
5.	Second Order Plot of Electron Disappearance in a Stoichiometric Propane/Air Flame at 1.0 atm. . . . .	36
6.	Effect of Chlorine on Negative-Particle Mobility in a Propane/Air Flame at 1.0 atm. . . . .	37

## SUMMARY

The concentration of positive ions and electrons in nominal 2000K hydrocarbon/air flames is  $10^{12}/\text{cm}^3$  at 1 atm. Ion concentration is  $10^5$  greater than that computed for equilibrium conditions. The important positive ions have been identified by sampling flames with a mass spectrometer. Using the mass spectrometer, chemical reactions which are responsible for the production and decay of positive ions and electrons have been identified and are



$\text{H}_3\text{O}^+$  is the major positive ion.

Data on negative ions is conflicting and it appears that the electron is the only negative ion of importance.

The rate of ion production was found to be  $10^{15} \text{ ions}/\text{cm}^3 \text{ sec atm}^2$ . The rate constant for positive ion decay was  $\approx 10^{-7} \text{ cm}^3/\text{sec}$  and is fairly insensitive to pressure and temperature over the ranges investigated. Rate constants for positive ion decay in flames seeded with alkali metals were found to be  $10^{-9} \text{ cm}^3/\text{sec}$ .

The effect of an electronegative gas (chlorine) on positive ion decay was investigated, and the rate was found to decrease about half an order of magnitude at a chlorine concentration of about 0.01 percent. Chlorine did not lower the amount of positive ions and free electrons in the flame reaction zone as compared with flames without chlorine. Experimental and analytical evidence indicates that electrons are attached by chlorine and that free electrons disappear at a faster rate by the attachment to electronegative species than by recombination with positive ions. The rate constant for attachment was taken to be  $10^{-29} \text{ cm}^6/\text{sec}$  which is a reasonable rate for three body ion-molecule reactions.

## LIST OF SYMBOLS

$e$	electron
$E_A$	electron affinity
$\Delta F$	free energy change
$g$	statistical weight
$\Delta H$	enthalpy change - includes heat of formation and heat capacity
$I_A$	ionization potential
$k$	a reaction rate constant
$K_p$	equilibrium constant
$M$	third body
$n$	number of ions
$p$	pressure
$R$	gas constant
$\Delta S$	entropy change
$t$	time
$T$	temperature
$X$	mole fraction
$Z$	volumetric collision rate
$\alpha$	recombination coefficient - a reaction rate constant involving ions and electrons
$[ \ ]$	concentration
$+$	(superscript) positive ion
$-$	(superscript) negative ion

## I. INTRODUCTION

Measurements of the concentration of ions in laboratory flames using air and hydrocarbon gases have shown that ion concentrations in the reaction zones are considerably higher than would be predicted from equilibrium considerations. Using various probing techniques, it has also been possible to measure the rate of decay of ions and electrons downstream of the flame reaction zone. Mass spectrometric sampling of laboratory flame gases have established the identity of the ions. Some measurements of the kinetics of electron attachment have also been attempted.

It is the purpose of this report to review the "ions in flames" aspect of the combustion literature. Since a flame is simply a reacting, flowing, radiating gaseous system, we would hope that information could be applied to the rates and nature of electron generation and decay in the boundary layers and wakes of hypersonic re-entry vehicles. Chemically speaking, the latter are also reacting, flowing, radiating gaseous systems. While the hydrodynamics of the situation will determine the structure of each type of "flame", basic aspects of physics and chemistry such as collision, reaction, radiation, etc., are common to both.

## II. ION CONCENTRATIONS IN FLAMES

The concentration of positive ions in the combustion zone of hydrocarbon/air flames at 1 atm was found to be  $10^{12}$  ions/cm<sup>3</sup> by several techniques (1-8). A typical schematic plot of ion concentration and position in the flame is shown in Figure 1. Such concentrations are many orders of magnitude greater than would be predicted from equilibrium considerations.

Thermal ionization in high temperature systems can be well approximated by the equation of Saha (9) wherein the position of equilibrium between an atom and its ions



is defined by

$$\log K_p = \frac{[X_{A^+ p}][X_e p]}{[X_A p]} \quad (2)$$

$$\log K_p = \frac{-218 I_A}{T} + 5/2 \log T - 6.5 + \log \left( \frac{g_e g_{A^+}}{g_A} \right)$$

The position of the equilibrium can also be derived by solution of the equilibrium constant for Eq. (1). This requires heat of formation, entropy, and heat capacity data for all constituents

$$2.3 \log K_p = \frac{-\Delta F}{RT} \quad (3)$$

$$= \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (4)$$

Comparing Eqs. (2) and (4), we can easily identify the statistical thermodynamic equivalent of  $(\Delta S/R)$  in Eq. (2) as well as the equivalence of the heat of reaction of Eq. (4) and the ionization potential of the atom.

Combustion products of hydrocarbon/air flames have as their normal constituents (present in mole fractions greater than  $10^{-8}$ ) those species which are listed in Table I. Also tabulated are the ionization potentials of the species, their concentrations at the listed adiabatic flame temperature, and their contribution to electron concentration as computed from Eq. (2). From examination of the Table we conclude that:

- a. From thermal equilibrium considerations, only NO can be considered as the primary source of electrons or positive ions
- b. The concentration of NO is too low by a factor of  $10^5$  to account for the amount of ions experimentally measured
- c. Contamination of the flame by  $10^{-8}$  mole fraction of an alkali metal such as sodium will produce 100 times the ionization of NO

It was shown that very lean propane/air flames which result in flame temperatures of 1300K yield ion concentrations of  $10^{10}$  ions/cm<sup>3</sup> (3, 4). At this temperature the ion contribution from NO is  $10^{-4}$  ions/cm<sup>3</sup>. To account for  $10^{10}$  ions/cm<sup>3</sup> at 1330K would require an alkali metal impurity of almost 0.01 mole fraction. It was concluded that the extreme excess of ionization was not due to the presence of contaminant alkali metals (3).

Not all flames yield excess ionization. Laboratory flames such as CS<sub>2</sub>/air and H<sub>2</sub>S/air with flame temperatures in excess of 2000K (3, 4), and H<sub>2</sub>/O<sub>2</sub>, H<sub>2</sub> + CO/O<sub>2</sub>, CH<sub>2</sub>O/O<sub>2</sub>, HCOOH/O<sub>2</sub>, H<sub>2</sub>S/O<sub>2</sub>, and CS<sub>2</sub>/O<sub>2</sub> (6) produced so few ions ( $\leq 10^5$  ions/cm<sup>3</sup>) that they were detected neither by electrical nor mass spectrometric measurement. The possibility of alkali metal contamination exists for these flames as well as the others, but these results appear to preclude contamination from all flames.

### III. NATURE OF EXCESS IONIZATION

In order to account for the excess ionization in hydrocarbon flames, Calcote (1) postulated the concept of chemi-ionization. In this approach one seeks a chemical reaction occurring in a flame which can lead to ionization. The thermodynamic probability of such a reaction occurring is related to the free energy change ( $\Delta F$ ) of the reaction which may be crudely approximated by the enthalpy change ( $\Delta H$ ) of the reaction. Thus to be considered thermodynamically feasible, the heats of these reactions should be approximately thermo-neutral or somewhat negative. Ionization energies (excluding alkali metals) range from 200 to 300 kcal/mole, while heats available from chemical reaction which result from the breaking and making of chemical bonds amount to no more than about 100 kcal/mole. Hence, conventional reactions leading to ionization will be highly endothermic and thermodynamically unlikely.

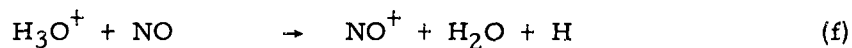
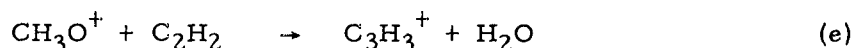
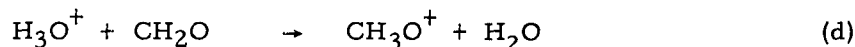
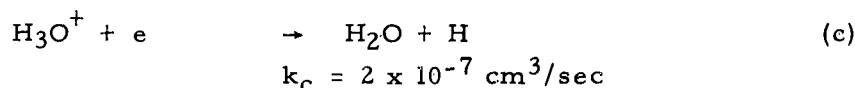
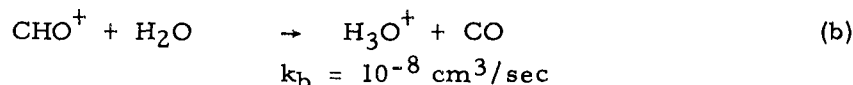
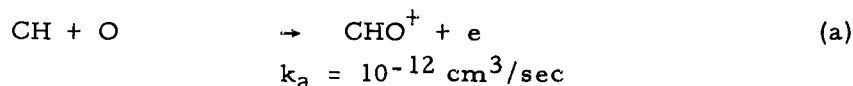
Highly energetic species (free radicals) such as  $C_2$  and  $CH$  have been detected by spectroscopy in the flame zone; these moieties are generally observed in an excited state (10). Table II lists some possible reactions involving free radicals and their excited states. It can be seen that reactions involving free radicals are sufficiently energetic to result in ionization.

#### IV. IDENTIFICATION OF IONS IN HYDROCARBON FLAMES

##### Positive Ions

A large number of mass spectrometric studies (11-19) have identified the important hydrocarbon flame ions by the sampling of laboratory flames. Figure 2 shows a typical plot of flame ion concentration as a function of distance above a burner. Flames were burned at 1 to 0.005 atm and there seemed to be no effect of pressure on the type or concentration of ions. For hydrocarbon/oxygen flames, major positive ions are  $\text{H}_3\text{O}^+$ ,  $\text{C}_3\text{H}_3^+$ ,  $\text{CHO}^+$ ; the first is most abundant, accounting for almost 90 percent of the ions.

Reactions such as (with their suggested rate constants);



are currently accepted to be responsible for the appearance and disappearance of various ions in hydrocarbon/oxygen flames; the mass-spectrometric work supports these mechanisms.

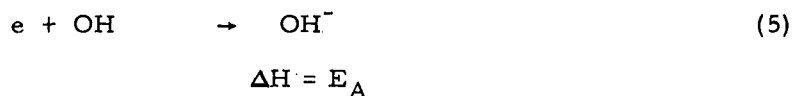
Reaction (a) is responsible for the initial formation of ions. Through reaction (b),  $\text{H}_3\text{O}^+$  is produced which is the major positive ion in hydrocarbon flames. Disappearance of ions through a dissociative recombination is shown in reaction (c). The minor ions are produced through reactions (d) and (e). Most significant is reaction (f); if NO is introduced into a flame containing  $\text{H}_3\text{O}^+$ ,



$\text{NO}^+$  is rapidly produced through a charge transfer reaction (16). When a nitrogen compound is added to the hydrocarbon/oxygen mixture either as fuel ( $\text{NH}_3$ ) or oxidizer ( $\text{N}_2\text{O}$ ), the most abundant ion becomes  $\text{NO}^+$  and accounts for 90 percent of the positive ions (17). Nitrogen introduced as a diluent ( $\text{N}_2$ ) will result in the formation of  $\text{NO}^+$  as a minor ion (15). Cyanogen flames produce  $\text{NO}^+$ , as do  $\text{NH}_3/\text{O}_2$  and  $\text{N}_2\text{O}/\text{H}_2$  flames (15).

#### Negative Ions

Kinbara and Ikegami (20) and King (21) found the mobilities associated with the negative ion of hydrocarbon flames to indicate the electron to be the important specie. Belcher and Sugden (22) introduced the idea that electron concentration might be significantly reduced by the attachment of electrons to hydroxyl radicals, to form negative hydroxyl ions, the former being the most electro-negative constituents of hydrocarbon flames



The idea received support from experimental work (23, 24, 25) which indicated an electron affinity ( $E_A$ ) of hydroxyl radicals to be about 60 kcal/mole. The photo-ionization work of Branscomb (26) suggests a much lower value of 40 kcal/mole.

Using 60 kcal for the electron affinity of OH, thermodynamic calculations show the ratio of electrons to  $\text{OH}^-$  to be 1.0 at 2000K and 1 atm; at 0.01 atm it is 100. For the lower value of 40 kcal for OH electron affinity, the ratios are  $10^2$  and  $10^4$ , respectively. From the conflicting data one cannot establish the importance of  $\text{OH}^-$ .

Recently Calcote (27) has modified the Langmuir probe to measure electron concentrations in hydrocarbon flames and finds that the ratio of positive ions to electrons is about 4. Thus he deduces that concentrations of negative ions are of the same order of magnitude as positive ions. The most reliable results appear to be the unpublished results (7) obtained using the Cambridge University mass spectrometer; negative ions were found to be unimportant.

## V. RATES OF PRODUCTION OF POSITIVE IONS

Using reactions (a)-(b) and their listed rates at steady state, the precursor positive ion may be accounted for by

$$\frac{d}{dt} [\text{CHO}^+] = 0 = k_a [\text{CH}] [\text{O}] - k_b [\text{CHO}^+] [\text{H}_2\text{O}] \quad (6)$$

Similarly, since  $[\text{H}_3\text{O}^+] = [\text{e}]$

$$\frac{d}{dt} [\text{H}_3\text{O}^+] = 0 = k_b [\text{CHO}^+] [\text{H}_2\text{O}] - k_c [\text{H}_3\text{O}^+]^2 \quad (7)$$

and we may write as the volumetric production rate of ions

$$k_a [\text{CH}] [\text{O}] = k_c [\text{H}_3\text{O}^+]^2 \quad (8)$$

$k_c$  has been found to be  $10^{-7}$  -  $10^{-8}$   $\text{cm}^3/\text{sec}$ , while  $[\text{H}_3\text{O}^+]$  at the maximum of the ion profile is  $10^{11}$  -  $10^{12}/\text{cm}^3$ . Thus the volumetric production rate is  $10^{15}$  -  $10^{16}$  ions/ $\text{cm}^3$  sec based on  $k_c$ . Based on  $k_a$  ( $10^{-12}$   $\text{cm}^3/\text{sec}$ ) and estimating  $[\text{CH}]$  and  $[\text{O}]$  to be  $10^{13}/\text{cm}^3$  and  $10^{15}/\text{cm}^3$  in the reaction zone (19), the volumetric production rate is  $10^{16}$  ions/ $\text{cm}^3$  sec.

In order to further check the rates, the volumetric bimolecular collision rate of CH and O at the above concentrations and at 2000K was computed

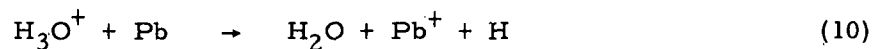
$$\begin{aligned} Z &= 7 \times 10^{-11} [\text{CH}] [\text{O}] \\ &= 10^{18}/\text{cm}^3 \text{ sec.} \end{aligned} \quad (9)$$

The observed rate of formation does not exceed the maximum rate predicted by collision theory.

Data taken from flames burning at 0.043 - 1.0 atm pressure indicate a volumetric rate of  $3 \times 10^{15}/\text{cm}^3 \text{ sec atm}^2$ , independent of pressure; data are summarized in Table III.

## VI. TRANSMITTED CHEMI-IONIZATION

Using a radio-frequency method to measure electron concentration, it was observed that traces of certain metals, particularly those with ionization potentials of about 175 kcal, give electron concentrations about 2 orders of magnitude greater than expected from the Saha equation in acetylene flames (28). The effect was most marked with lead and the electron concentration was observed to decrease downstream of the reaction zone according to a second order law, but with a much smaller rate constant than  $10^{-7}$  cm<sup>3</sup>/sec (29). The explanation was advanced that electron-ion recombination occurs following chemi-ionization in the reaction zone. Metal ions such as lead (Pb) result from electron transfer from ordinary flame ions



These atomic ions combine with electrons more slowly than the dissociative recombination occurs since a third body is necessary.

## VII. POSITIVE ION RECOMBINATION IN FLAMES

Since the rate of ionic recombination in a flame is proportional to the concentration of positive ions and electrons, we may write as in second order kinetics

$$dn^+ = -\alpha n^+ n^- dt \quad (11)$$

Electroneutrality is preserved

$$n^+ = n^- \quad (12)$$

and after integration, assuming  $n_0^+$  initial positive ions

$$1/n^+ = \alpha t + 1/n_0^+ \quad (13)$$

From the latter equation we see that a plot of reciprocal ion concentration versus time should yield a straight line. The slope of the line will yield  $\alpha$  which is usually called the recombination coefficient. Time is usually computed from the position of an ionic probe in the flame and flame gas flow rate. For first order kinetics, Eq. (13) is

$$2.3 \log \left( \frac{n_0^+}{n^+} \right) = \alpha t \quad (14)$$

and a plot of log ion concentration versus time should yield a straight line of slope  $\alpha$ .

### Hydrocarbon Flames

Wilson (30) deduced a value of  $8.5 \times 10^{-7} \text{ cm}^3/\text{sec}$  for the recombination coefficient in a flame from conductivity data. Using Langmuir probe techniques, King (31) found  $\alpha$  to be  $2.5 \times 10^{-7} \text{ cm}^3/\text{sec}$  in a methane/air flame burning at 0.087 atm. Flames are usually burned at reduced pressure in order to increase the length of the flame in which ion recombination takes place and thus the precision of recombination measurements. The usual technique using the Langmuir probe is to measure ion concentration at various stations downstream from the reaction zone.

King's results agree well with results (32) obtained with microwave observations on an electrodeless discharge in helium where  $\alpha$  was found to be  $2 \times 10^{-8}$  cm<sup>3</sup>/sec. Bates (33) has interpreted the results of (32) to indicate that electron decay occurs through dissociative recombination where an electron neutralizes a positive molecular ion.

Measurements (34) in a propane/air flame at 1 atm between 1600-2000K yielded a recombination coefficient of  $0.6 \times 10^{-7}$  cm<sup>3</sup>/sec; the order of magnitude of  $\alpha$  indicates that either third body or dissociative recombination must be the predominant process by which ions decay in a flame.  $\alpha$  was also found to increase slightly with increasing temperature. Calcote (35) found  $\alpha$  to be  $1.6 \times 10^{-7}$  cm<sup>3</sup>/sec in propane/air flames burned at 0.043 and 0.087 atm and independent of pressure when  $\alpha$  was corrected for ambipolar diffusion.

King (21) found  $\alpha$  to be  $2.9 \times 10^{-7}$  cm<sup>3</sup>/sec for propane/air at 0.072 atm and  $2.8 \times 10^{-7}$  cm<sup>3</sup>/sec for acetylene/air at 0.026 atm. In the former case, the logarithm of the recombination coefficient varied inversely as the logarithm of the pressure, giving a negative pressure index of -0.64. Green and Sugden (19) found  $\alpha$  to be  $2.2 \times 10^{-7}$  cm<sup>3</sup>/sec by mass spectrometrically following the decay of  $\text{H}_3\text{O}^+$  in  $\text{O}_2/\text{H}_2/\text{N}_2$  flames containing about 1 percent acetylene.

#### Alkali Metal Flames

Alkali metal salts ionize to an abnormal extent through the process of transmitted chemi-ionization when introduced into a hydrocarbon flame. Ionization in the reaction zone is greater than that predicted from thermal considerations, and decay of abnormal ionization permits measurement of the recombination coefficient. King (36) measured the recombination coefficients of several alkali metals by atomizing dilute solutions of their salts into a propane/air flame at 1 atm and 1970K. Using a Langmuir probe, he found  $\alpha$  to be  $6 \times 10^{-10}$ ,  $4 \times 10^{-9}$ , and  $9 \times 10^{-9}$  cm<sup>3</sup>/sec for potassium, sodium, and lithium, respectively. These agreed well with values of  $3.5 \times 10^{-9}$  and  $5.5 \times 10^{-9}$  cm<sup>3</sup>/sec which were found for sodium and lithium (37) using electromagnetic attenuation measurements in a 2400K flame.

Thus experimental evidence shows that recombination coefficients in flames containing alkali metal salts are two orders of magnitude smaller than those for natural flame ions. Neutralization in alkali metal flames would be expected to follow a three body process



Coefficients derived from experiments (36 - 37) resulted from assuming a second order process for neutralization. The three body reaction rate constant for Eq. (15) is about  $10^{-27} \text{ cm}^6/\text{sec}$  (38). Assuming a third body concentration at 2000K of  $M \cong 10^{18}/\text{cm}^3$ , we derive a second order recombination coefficient for Eq. (15) of approximately  $10^{-9} \text{ cm}^3/\text{sec}$  which agrees well with the experimental data.

## VIII. EFFECT OF ELECTRONEGATIVE GASES ON FLAME IONS

### Thermodynamic Considerations

When an electronegative gas (electron attracting) is introduced into a flame, thermodynamic considerations show that many of the free electrons created by the combustion process should become attached to these electronegative gases to form negative ions.

The fraction of free electrons attached will depend on the "strength" of the electron-radical bond which is the electron affinity. Table IV lists the electron affinities of some electronegative gases and radicals. As shown previously, the electron affinity of OH (60 kcal) was such that the ratio  $e/OH^-$  under equilibrium conditions in a hydrocarbon/air flame at 2000K and 1 atm was approximately 1. With the larger attachment energies of the halogens, we calculate the ratio  $e/Cl^-$  to be  $10^{-5}$  in a similar flame containing 0.2 percent chlorine atoms. Thus under equilibrium conditions we find that small amounts of electronegative species can attach large fractions of free electrons. Since there is already an enormous amount of ionic non-equilibrium in the reaction zone of flames, it would seem that the amount of electron attachment would depend strongly on the kinetics of the attachment process and predictions based on equilibrium concepts are not justified.

### Experimental Results

Little experimental work has been reported on the effects of electronegative gases. Van Tiggelen (15) has shown that the combustion of nitrogen/oxygen/vinyl chloride ( $CH_2CHCl$ ) flames produces essentially the same amount of ionization as found with oxygen/hydrocarbon flames. His apparatus, the circular slit burner, measures the flame conductivity in the reaction zone. Since electrons alone are responsible for flame conductivity, it is obvious that electronegative constituents do not prevent the formation of excess concentrations of electrons in the reaction zone. Mass spectrometric analysis of the same

flame (19) has shown that  $\text{H}_3\text{O}^+$  remains the predominant positive ion;  $\text{H}_3\text{O}_2^+$  and  $\text{H}_2\text{Cl}^+$  appear as new ions. Relative ratios of  $\text{H}_3\text{O}^+/\text{H}_3\text{O}_2^+/\text{H}_2\text{Cl}^+/\text{NO}^+$  were 100/22/20/15. Essentially the same results were found when hydrogen bromide (HBr) was added to acetylene flames.

King (21) investigated the effects of electronegative gases on air/propane flames at 1 atm by the addition of small amounts of  $\text{CHCl}_3$ . He noted an increase in the number of positive ions over that observed in flames without additives.

The phenomenon is easily explained; the steady state between positive ions and electrons must be preserved while electrons are removed by attachment to chlorine - thus the total number of positive ions must increase. On the other hand, Padley (39) found that addition of small amounts of chlorine to an alkali metal containing flame increased the electron concentration 1 inch from the reaction zone as compared to the flame without additive. The phenomena was explained by the reaction



The results of King's work (21) on the decay of positive ions in the presence of electronegative gases are shown in Figure 3. The decrease in  $\alpha$  was about one-half order of magnitude. It is surprising that recombination coefficients are reduced by the addition of chlorine since ion-ion reactions could be taken to proceed at a rate more rapid than ion-electron reactions (40).

Since King (21) used a Langmuir probe which could only determine positive ion decay, nothing could be deduced about the decay of electrons. King (21) also studied the disappearance of electrons in the same flames using an electromagnetic attenuation technique (41). He found that electrons decayed in flames both with and without halogen additives as a first order process (Figure 4) rather than a second order process (Figure 5). King's results on the flame containing no additive agreed with those of Williams (41, 42) who found that electrons in hydrocarbon flames disappear by a first order process. Furthermore, the mobilities (Figure 6) of the negative ions were measured with and without electronegative additives and were found to decrease by 2



orders of magnitude some 5 cm above the flame zone with additives. From the mobility data one can only assume that electrons are attached by chlorine in the additive. These data are not at variance with those of Van Tiggelen (15) who showed that even with enormous amounts of chlorine,  $10^{12}$  electrons/cm<sup>3</sup> were produced in the reaction zone. On the other hand, King showed that electrons were attached in the area above the reaction zone.

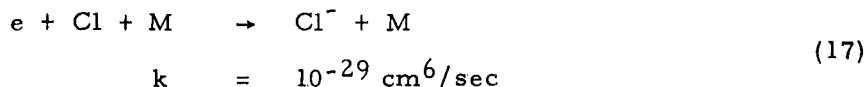
In a later publication, King (43) investigated the effects of small amounts of CCl<sub>4</sub> in reducing free electron concentration in alkali metal seeded air/CO flames at 2000K and 1 atm. The air/CO flame produces no flame ions of its own and it was shown that the effectiveness of electron reduction decreases as the ionization potential of the alkali metal increases. The ratios of recombination coefficients were determined in an alkali metal seeded air/propane flame at 1840K and 1 atm with and without CCl<sub>4</sub> additive. Results are summarized in Tables V and VI.

#### Analysis of Experimental Results

It has been shown that Cl atoms are thermodynamically capable of attaching significant amounts of free electrons. It would be interesting to predict whether the kinetics of the process are such that the reaction can proceed with a measureable rate. It would also be significant to show how the attachment process, which is in reality a three body reaction, can yield first order kinetics as derived from flame measurements by King (21).

Of further significance would be the illustration that attachment can take place at a rate equal to or faster than recombination, which would constitute a further proof for attachment. Both chlorine atoms and H<sub>3</sub>O<sup>+</sup> ions compete for electrons. If attachment is more rapid than recombination, electrons will disappear by a first order process (attachment). If recombination is more rapid, then electrons will disappear by a second order process (recombination).

The three body attachment reaction



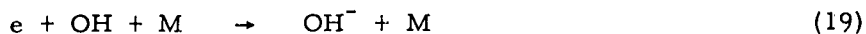
at 2000K and 1 atm ( $M \cong 10^{18}/\text{cm}^3$ ) should exhibit second order kinetics with

$$k = 10^{-11} \text{ cm}^3/\text{sec} \quad (18)$$

If the concentration of chlorine atoms is much greater than the concentration of electrons, then pseudo-first order kinetics will be observed. Assuming  $[Cl] = 10^{15}/\text{cm}^3$  and  $[e] = 10^{12}/\text{cm}^3$ , electrons will become attached as  $e^{-10^4 t}$ ;  $10^{-4}$  sec is required to reduce electron concentration to 1/10. For  $[e] = [H_3O^+] = 10^{12}/\text{cm}^3$  the second order positive ion-electron recombination reaction will require  $10^{-3}$  sec to reduce electron concentration to 1/10 using  $k \cong 10^{-8} \text{ cm}^3/\text{sec}$  as measured by King (21). For  $[e] = [H_3O^+] = 10^{11}/\text{cm}^3$ , the recombination reaction will require  $10^{-2}$  sec to reduce electron concentration to 1/10.

Thus it has been shown that three body electron attachment can proceed at a faster rate than recombination in the presence of electronegative gases. Furthermore, the attachment process should exhibit first order kinetics. Recombination can then take place between positive ions and both electrons and negative ions and positive ion decay will exhibit second order kinetics.

King (21), as shown in Figure 4, found that electrons decayed by a first order process in a propane/air flame which suggests three body electron attachment to OH



Using a rate constant of  $10^{-29} \text{ cm}^6/\text{sec}$ , assuming  $[M] = 10^{18}/\text{cm}^3$ ,  $[e] = 10^{12}/\text{cm}^3$ , and  $[OH] = 10^{14}/\text{cm}^3$ , we find that electron concentration will be reduced by 1/10 in  $10^{-3}$  sec through attachment. For  $[e] = 10^{12}/\text{cm}^3$  and  $10^{11}/\text{cm}^3$ , electron concentration should decay through recombination by

a factor of 10 in  $10^{-4}$  sec and  $10^{-3}$  sec, respectively. We conclude that decay of electrons by attachment and recombination can apparently take place in air/hydrocarbon flames at comparable rates. Unfortunately, the uncertainty in electron affinity of OH, the generally contradictory experimental results, and the inconclusive kinetic calculations do not permit proper assessment of electron attachment to OH.

## BIBLIOGRAPHY

1. Calcote, H. F., Third International Symposium on Combustion, p. 245, The Williams and Wilkins Company, Baltimore, 1949.
2. Calcote, H. F., and Pease, R. W., Ind. Eng. Chem., 43, 2726 (1951).
3. Calcote, H. F. and King, I. R., 5th International Symposium on Combustion, p. 423, Reinhold Publishing Company, New York, 1955.
4. King, I. R., and Calcote, H. F., J. Chem. Phys., 23, 2203 (1955).
5. King, I. R., J. Chem. Phys., 31, 855 (1959).
6. Van Tiggelen, A., "Ionization Phenomena in Flames," Paper presented at the ARS Conference, Palm Springs, California, October 10, 1962. See also ASTIA No. 258050.
7. Sugden, T. M., "A Survey of Flame Ionization Work at the University of Cambridge", Paper presented at the ARS Conference, Palm Springs, California, October 10, 1962.
8. Calcote, H. F., Combustion and Flame, 1, 385 (1957).
9. Saha, H., Phil. Mag. 40, 472 (1920).
10. Gaydon, A. G., and Wolfhard, H. G., Flames, p. 227, Chapman and Hall Co., London, 1962.
11. Deckers, J., and Van Tiggelen, A., Bull. Soc. Chem. Belg., 66, 664 (1957), Nature, 181, 1460 (1958), ibid 182, 863 (1958).
12. Knewstubb, P. F., and Sugden, T. M., Nature, 181, 474 (1958).
13. Knewstubb, P. F., and Sugden, T. M., Seventh International Symposium on Combustion, p. 247, Butterworths Scientific Publications, London, 1959.
14. Deckers, J., and Van Tiggelen, A., Seventh International Symposium on Combustion, p. 254, Butterworths Scientific Publications, London, 1959.

#### BIBLIOGRAPHY (Continued)

15. Van Tiggelen, A., Ion Identification and Analyses in Flames, May 1960 (ASTIA-242292), May 1961 (ASTIA-258050), May 1962 (ASTIA-278417).
16. Knewstubb, P. F., and Sugden, T. M., Proc. Roy Soc., London A255, 520 (1960).
17. De Jaegere, S., et al., Eighth International Symposium on Combustion, p. 254, The Williams and Wilkins Company, Baltimore, 1962.
18. Bascombe, K. N., et al., Joint Symposium on Mass Spectrometry, ASTM and Institute of Petroleum Oxford, 1961; Pergamon Press Ltd., Oxford, 1962.
19. Green, J. A., and Sugden, T. M., Ninth International Symposium on Combustion, Cornell Univ., Ithaca, New York, August 27, 1962.
20. Kinbara, T., and Ikegami, H., Combustion and Flame, 1, 199 (1957).
21. King, I. R., J. Chem. Phys., 37, 74 (1962).
22. Belcher, H. E., and Sugden, T. M., Proc. Roy. Soc. A, 202, 17 (1950).
23. Smith, H., and Sugden, T. M., Proc. Roy. Soc. A, 211, 31 (1952).
24. Smith, H., and Sugden, T. M., Proc. Roy. Soc. A, 211, 58 (1952).
25. Page, F. M., Disc. Faraday Soc., 19, 87 (1955).
26. Branscomb, L. M., Advances in Electronics and Electron Physics, p. 66, Academic Press, Inc., New York City, 1957.
27. Calcote, H. F., Ninth International Symposium on Combustion, Cornell Univ., Ithaca, New York, August 27, 1962.
28. Knewstubb, P. F., and Sugden, T. M., Research Correspondence (London) 9, A1 (1956).
29. Padley, P. J., and Sugden, T. M., Eighth International Symposium on Combustion, p. 164, The Williams and Wilkins Company, Baltimore, 1962.

# BIBLIOGRAPHY (Continued)

30. Wilson, H. A., Revs. Modern Phys. 3, 156 (1931).
31. King, I. R., J. Chem. Phys. 27, 817 (1957).
32. Biondi, M. A., and Brown, S. C., Phys. Rev., 76, 1697 (1949).
33. Bates, D. R., Phys. Rev. 77, 718 (1950); 78, 492 (1950).
34. King, I. R., J. Chem. Phys., 35, 380 (1961).
35. Calcote, H. F., Eighth International Symposium on Combustion, p. 184, The Williams and Wilkins Company, Baltimore, 1962.
36. King, I. R., J. Chem. Phys., 36, 553 (1962).
37. Knewstubb, P. E., and Sugden, T. M., Trans. Faraday Soc., 54, 372 (1958).
38. Bortner, M. H., and Baulknight, C. W., "Deionization Kinetics," July 1961; Missile and Space Vehicle Department, General Electric Company, Philadelphia.
39. Padley, P. J., et al., Trans Faraday, Soc., 57, 1552 (1961).
40. Loeb, L. B., Basic Process of Gaseous Electronics, University of California Press, Berkeley, California, 1955.
41. Williams, H., Seventh Symposium on Combustion, p. 269, Butterworth's Scientific Publications Ltd., London, 1957.
42. Williams, H., Eighth International Symposium on Combustion, p. 179, The Williams and Wilkins Company, Baltimore, 1962.
43. King, I. R., "Recombination of Ions in Flames", Paper presented at ARS Conference, Palm Springs, California, October 10, 1962.

TABLE I  
Equilibrium Combustion Products of the Stoichiometric<sup>1</sup> Cyclohexane/Air  
Flame (2200K)

Product	Product <sup>2</sup> Concentration (mole fraction)	Ionization Potential (kcal)	Electron Concentration (mole fraction)	(electrons/cm <sup>3</sup> )
H	2.55E-04	313	4.2E-18	1.4E+01
O	1.82E-04	313	3.5E-18	1.2E+01
OH	1.82E-04	306	2.1E-16	7.0E+02
H <sub>2</sub> O	1.21E-01	290	1.2E-14	4.0E+04
H <sub>2</sub>	2.05E-03	354	8.8E-19	2.9E+00
CO	1.00E-02	322	7.7E-17	2.6E+02
CO <sub>2</sub>	1.14E-01	317	4.4E-16	1.4E+03
NO	1.91E-03	213	9.4E-12	3.1E+07
N <sub>2</sub>	7.43E-01	359	9.7E-18	3.2E+01
O <sub>2</sub>	4.60E-03	370	2.0E-17	6.7E+01
(Na)	(1.00E-08)	118	(1.0E-09)	(3.3E+09)

1.  $\text{CH}_2 + 3/2 (\text{O}_2 + 4\text{N}_2) \longrightarrow \text{CO}_2 + \text{H}_2\text{O} + 6\text{N}_2$
2. 2.55E-04 is  $2.55 \times 10^{-4}$

TABLE II  
Possible Chemi-ionization Reactions

<u>Reaction</u>	<u>Heat of Reaction (<math>\Delta H</math> - kcal)</u>
$\text{CH} + \text{O} \longrightarrow \text{CHO}^+ + \text{e}$	$\approx 0$
$\text{CH}^* + \text{O} \longrightarrow \text{CHO}^+ + \text{e}$	- 69
$\text{C}_2^* + \text{OH} \longrightarrow \text{CH}^+ + \text{CO} + \text{e}$	- 10
$\text{C}_2^* + \text{O}_2 \longrightarrow \text{CO}^+ + \text{CO} + \text{e}$	- 20
$\text{CH} + \text{O}_2^* \longrightarrow \text{CHO}_2^+ + \text{e}$	-110
$\text{CH}^* + \text{O}_2 \longrightarrow \text{CHO}_2^+ + \text{e}$	- 30

\*Excited state



TABLE III  
Rates of Ion Formation in Propane/Air Flames

<u>Pressure (atm)</u>	<u>Recombination Coefficient (cm<sup>3</sup>/sec)</u>	<u>Production Rate (cm<sup>-3</sup> sec<sup>-1</sup>)</u>	<u>Rate Divided by (Pressure)<sup>2</sup> (cm<sup>-3</sup> sec<sup>-1</sup> atm<sup>-2</sup>)</u>	<u>Reference</u>
0.043	$1.6 \times 10^{-7}$	$5.6 \times 10^{12}$	$3.0 \times 10^{15}$	(27)
0.087	$2.4 \times 10^{-7}$	$2.8 \times 10^{13}$	$3.7 \times 10^{15}$	(27)
0.27	$1.6 \times 10^{-7}$	$2.1 \times 10^{15}$	$2.9 \times 10^{15}$	Unpublished results, I. R. King, Experi- ment Inc.
1.0	$2 \times 10^{-7}$	$2 \times 10^{15}$	$2 \times 10^{15}$	(8)

I

TABLE IV  
Electron Affinities

<u>Species</u>	<u>Electron Affinity</u> <u>(<math>E_A</math> - kcal/mole)</u>
Cl	87.6
F	80.7
I	73.8
O	33.7
O <sub>2</sub>	9.2
OH	60 (?)

TABLE V

Effect of Carbon Tetrachloride in Reducing Free-Electron  
Concentrations (Ne) in a Carbon Monoxide/Air Flame at  
1 Atm and a Flame Temperature of 2000K. (42)

Salt	Ne <sub>1</sub> (without Additive)	Ne <sub>2</sub> (with Additive)	Ne <sub>1</sub> /Ne <sub>2</sub>
0.001 N Cs <sub>2</sub> CO <sub>3</sub>	34.6 x 10 <sup>10</sup>	5.5 x 10 <sup>9</sup>	62
0.0001 N Cs <sub>2</sub> CO <sub>3</sub>	10.9	2.7	40
0.001 N K <sub>2</sub> CO <sub>3</sub>	8.9	3.3	27
0.0001 N K <sub>2</sub> CO <sub>3</sub>	2.8	1.5	19
0.01 N Na <sub>2</sub> CO <sub>3</sub>	2.68	5.2	5
0.001 N Na <sub>2</sub> CO <sub>3</sub>	0.81	2.5	3.2
0.0001 N Na <sub>2</sub> CO <sub>3</sub>	0.25	1.95	1.3
0.1 N Li <sub>2</sub> CO <sub>3</sub>	4.1	5.0	8
0.01 N Li <sub>2</sub> CO <sub>3</sub>	1.3	3.3	4

TABLE VI  
Effect of Carbon Tetrachloride on Recombination Rates ( $\alpha$ )  
of Alkali-metal Ions in a Propane/Air Flame at 1 Atm  
and a Flame Temperature of 1840K (42)

Alkali Metal	$\alpha(\text{salt})/\alpha(\text{salt} + \text{CCl}_4)^a$	Ionization Potential, ev
Li	0.75	5.36
Na	1.3	5.12
K	8.0	4.318
Rb	2.0	4.159
Cs	5.5	3.87

<sup>a</sup>Values given are average values; 0.02 percent by volume of carbon tetrachloride vapor was added to the total flow in all cases.

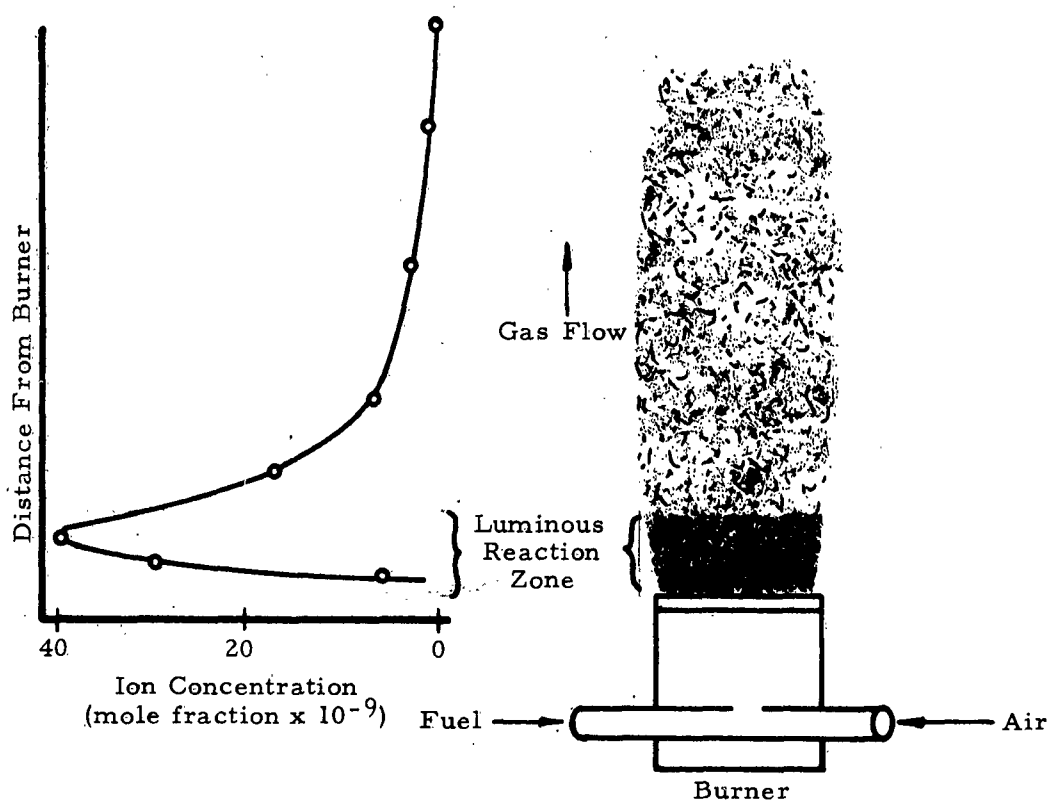


Figure 1. Typical Plot of Ion Concentration in a Laboratory Flame

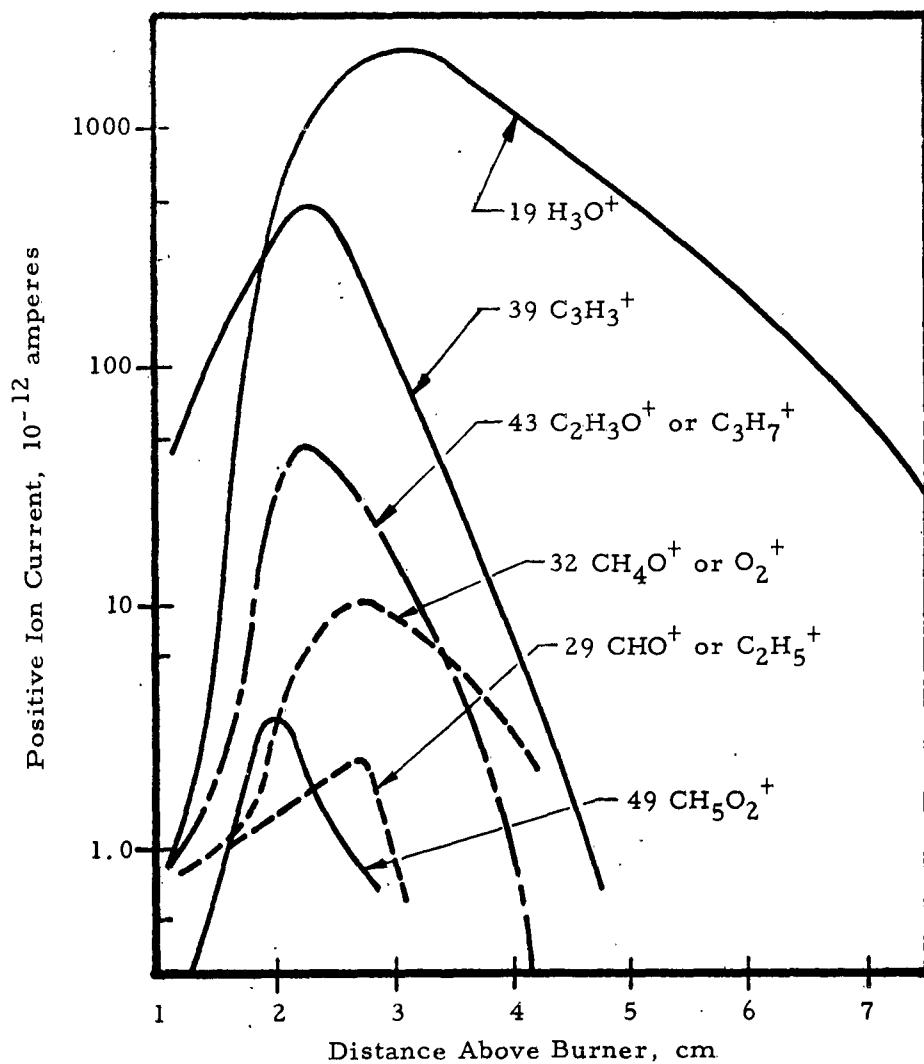


Figure 2. Ion Concentration Profiles for an Acetylene/Oxygen Flame (27)  
pressure = 0.0032 atm

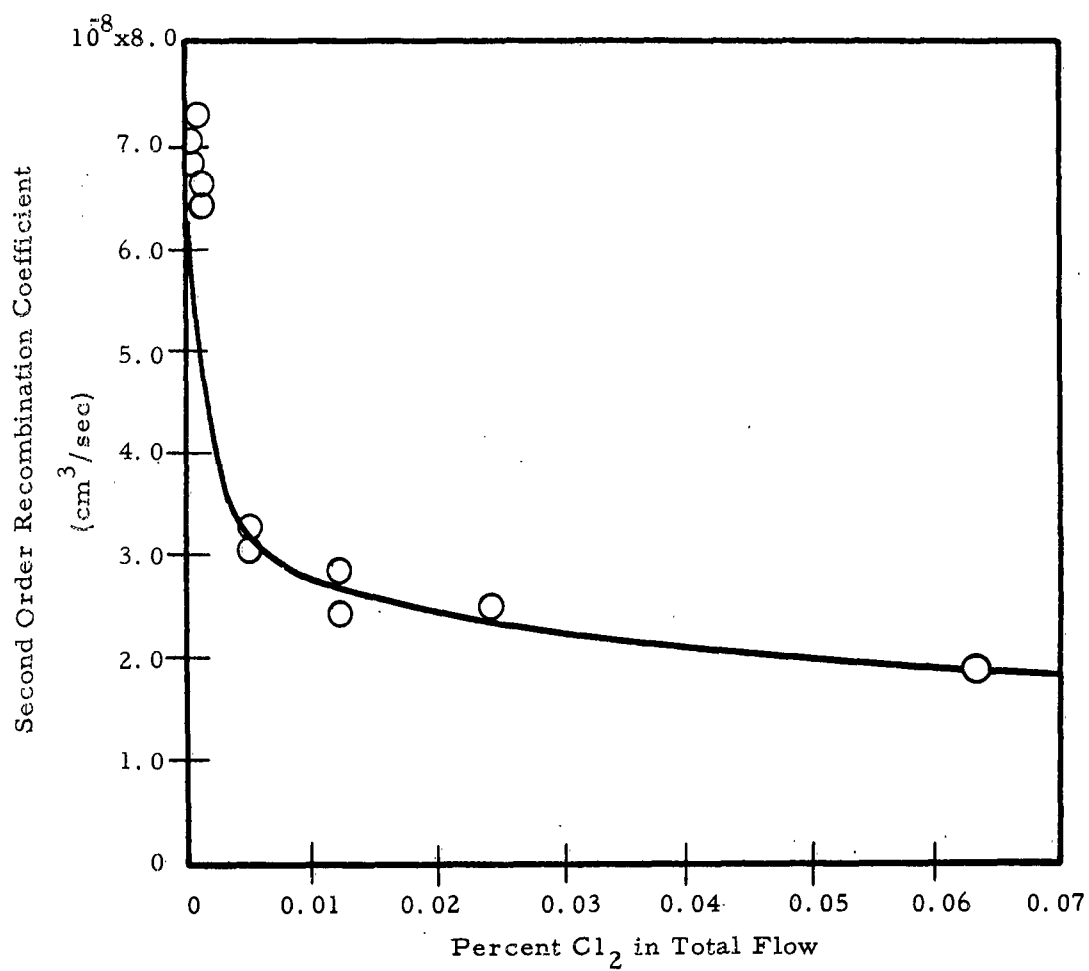


Figure 3. Effect of Chlorine on Recombination in a Propane/Air Flame at 1.0 Atm. (21)

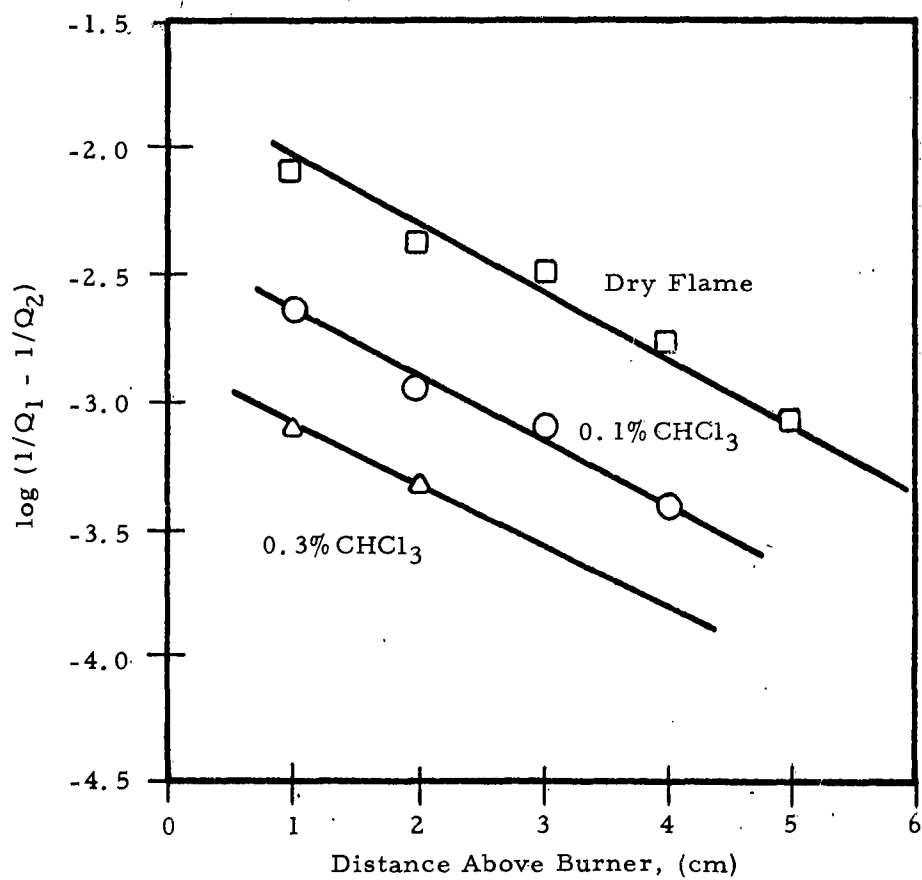


Figure 4. First Order Plot of Electron Disappearance in a Stoichiometric Propane/Air Flame at 1.0 atm (21)



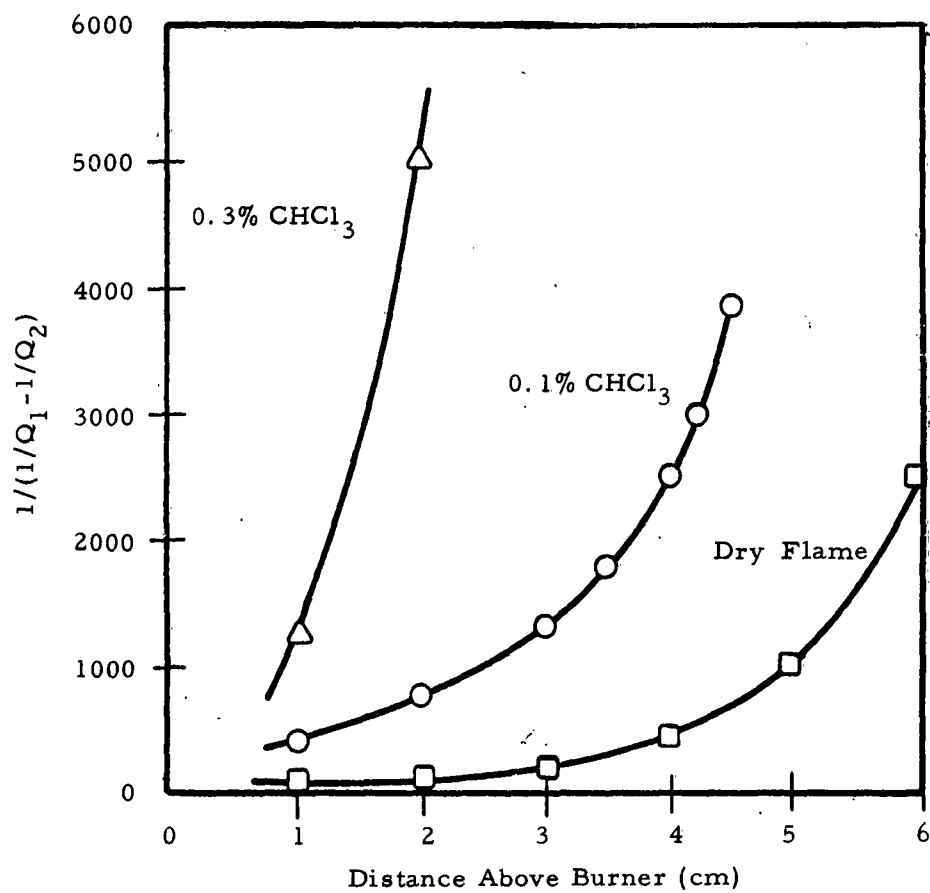


Figure 5. Second-order Plot of Electron Disappearance in a Stoichiometric Propane/Air Flame at 1.0 atm. (21)

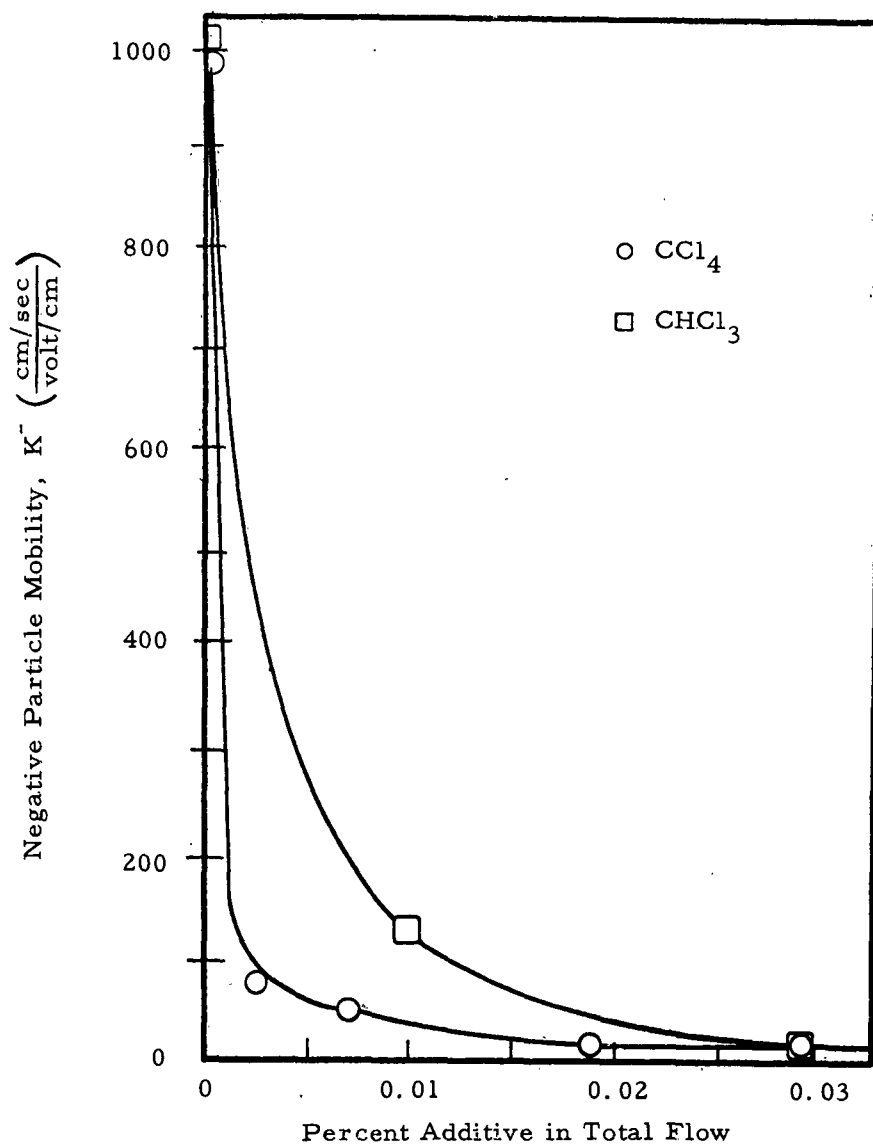


Figure 6. Effect of Chlorine on Negative-particle Mobility in a Propane/Air Flame at 1.0 atm. (21)

## AEROSPACE CORPORATION

## TECHNICAL REPORTS - DISTRIBUTION LIST

## REPORT TITLE

A LITERATURE SURVEY OF IONS IN FLAMES

## REPORT NO.

TDR-169(S3153-01)TN-5

## DATE

15 June 1963

## SECURITY CATEGORY

UNCLASSIFIED

## INTERNAL DISTRIBUTION

SBO

Batdorf, S. B.  
Claflin, H. C.  
Dorrance, W. H.  
Fitzgerald, F. F.  
Fowler, R. G.  
Garblik, A. M.  
Green, A.  
Greene, S. A. (20)  
Henshall, B. D.  
Hill, J. A.  
Levinsky, E. S.  
Li, F. K.  
Millburn, G. P.  
Pearce, K.  
Sullivan, H. C.  
Weeks, I. F.  
Whalen, R. J.

ESO

Colwell, J. E.  
Hartunian, R. A.  
Heicklen, J. P.  
Hove, J. E.  
Myers, H. A.  
O'Shaughnessy, M. T.  
Wachi, F. M.  
Wilkins, R. L.

PREPARED BY

## AEROSPACE CORPORATION

## TECHNICAL REPORTS - DISTRIBUTION LIST

REPORT TITLE

A LITERATURE SURVEY OF IONS IN FLAMES

REPORT NO.

TDR-169(S3153-01)TN-5

DATE

15 June 1963

SECURITY CATEGORY

UNCLASSIFIED

## EXTERNAL DISTRIBUTION

MILITARY AND GOVERNMENT OFFICES

ASSOCIATE CONTRACTORS AND OTHER

BSD

Jefferson, K. G.

Levy, W. C.

Mauldin, M.

Defense Documentation Center

Reference Office

Arlington Hall Station

Arlington 12, Virginia

Attn: TISIA

## INSTRUCTIONS

WHEN APPROVED BY GOVERNMENT PROGRAM OFFICE, LINE OUT UNUSED SPACE TO PRECLUDE ADDITIONAL ENTRIES.

PREPARED BY

(FOR AEROSPACE CORPORATION)

APPROVED BY

(FOR GOVERNMENT PROGRAM OFFICE)

<p>Aerospace Corporation, San Bernardino Operations. A LITERATURE SURVEY OF IONS IN FLAMES. Prepared by S. A. Greene, Aerospace Mechanics Subdivision. 15 June 1963. [45] p. incl. illus. (Report TDR-169(S3153-01)TN-5;BSD-TDR-63-105) (Contract AF 04(695)-169) Unclassified report</p> <p>The literature on the "ions in flames" aspects of combustion in laboratory flames was reviewed. The nature of excess non-equilibrium ionization and rates of ionization are discussed. Rates for positive ion decay are presented as well as the effects of electronegative gases on amounts of ionization, rates of positive ion and electron decay, and rates of electron attachment.</p>	UNCLASSIFIED
--	--------------

<p>Aerospace Corporation, San Bernardino Operations. A LITERATURE SURVEY OF IONS IN FLAMES. Prepared by S. A. Greene, Aerospace Mechanics Subdivision. 15 June 1963. [45] p. incl. illus. (Report TDR-169(S3153-01)TN-5;BSD-TDR-63-105) (Contract AF 04(695)-169) Unclassified report</p> <p>The literature on the "ions in flames" aspects of combustion in laboratory flames was reviewed. The nature of excess non-equilibrium ionization and rates of ionization are discussed. Rates for positive ion decay are presented as well as the effects of electronegative gases on amounts of ionization, rates of positive ion and electron decay, and rates of electron attachment.</p>	UNCLASSIFIED
--	--------------

<p>Aerospace Corporation, San Bernardino Operations. A LITERATURE SURVEY OF IONS IN FLAMES. Prepared by S. A. Greene, Aerospace Mechanics Subdivision. 15 June 1963. [45] p. incl. illus. (Report TDR-169(S3153-01)TN-5;BSD-TDR-63-105) (Contract AF 04(695)-169) Unclassified report</p> <p>The literature on the "ions in flames" aspects of combustion in laboratory flames was reviewed. The nature of excess non-equilibrium ionization and rates of ionization are discussed. Rates for positive ion decay are presented as well as the effects of electronegative gases on amounts of ionization, rates of positive ion and electron decay, and rates of electron attachment.</p>	UNCLASSIFIED
--	--------------

<p>Aerospace Corporation, San Bernardino Operations. A LITERATURE SURVEY OF IONS IN FLAMES. Prepared by S. A. Greene, Aerospace Mechanics Subdivision. 15 June 1963. [45] p. incl. illus. (Report TDR-169(S3153-01)TN-5;BSD-TDR-63-105) (Contract AF 04(695)-169) Unclassified report</p> <p>The literature on the "ions in flames" aspects of combustion in laboratory flames was reviewed. The nature of excess non-equilibrium ionization and rates of ionization are discussed. Rates for positive ion decay are presented as well as the effects of electronegative gases on amounts of ionization, rates of positive ion and electron decay, and rates of electron attachment.</p>	UNCLASSIFIED
--	--------------